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Communications to the Editor

Butatriene-Based Polymer Chemistry. 3.[1] New Route to Substituted Poly(acetylene)s through the Base-Catalyzed Rearrangement of Poly(2-butyne-1,4-diyl)s

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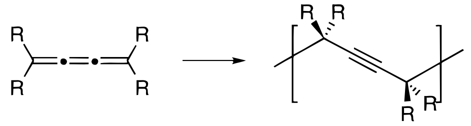
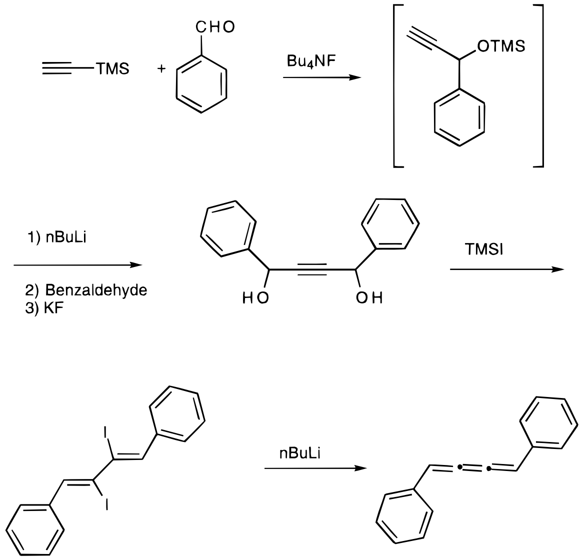
Introduction. The polymerization of simple butatrienes has long frustrated spectroscopists in their attempts to isolate and study the free monomeric molecule.[2−7] Carothers observed this phenomenon and obtained a patent on the potential use of butatriene as a reactive monomer, not understanding the nature of the polymer formed.[8] Recently, we have been studying the structure and potential applications of butatrienes as monomers in addition polymerization.[9−11] In reviewing of the literature concerning 1,2,3-butatriene, there were reports that in some situations, the normally white solid formed from its polymerization would convert to a yellow, blue or even black material.[2] This intrigued us as it implied the formation of a conjugated system. On the basis of our previous and ongoing studies, 1,2,3-butatrienes polymerize in the presence or absence of free-radical initiators via a 1,4-addition to produce a poly(2-butyne-1,4-diyl) structure.



For the case R=H, this creates a polymer which is formally $(C_4H_4)_n$. This is isomeric with the conjugated polymer poly(acetylene). We reasoned that the formation of colored materials could be due to rearrangement of the unconjugated, acetylene-containing system to the thermodynamically more stable conjugated polyene. If one could design the butatriene monomer appropriately, such a rearrangement of the resulting substituted poly(2-butyne-1,4-diyl) could lead to conjugated polymers with unique electronic and physical properties. In this paper, we report on the first example of such a rearrangement.

Results and Discussion. We chose 1,4-diphenyl-1,2,3-butatriene (**1**) as our initial 1,4-disubstituted butatriene. We felt that the presence of the aromatic groups would serve to stabilize the cumulene enough that its polymerization could be controlled. A number of workers have reported the synthesis of **1**.[12−15] Our approach was the formation of 1,4-diphenyl-1,4-dihydroxy-2-butyne via a two-step one-pot reaction of trimethylsilylacetylene with benzaldehyde.[16] The diol is then treated with iodotrimethylsilane to provide 2,3-diodo-1,4-diphenylbutadiene and reductive elimination with n-BuLi afforded *trans*-1,4-diphenyl-1,2,3-butatriene in good yield.



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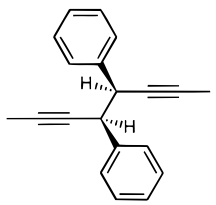
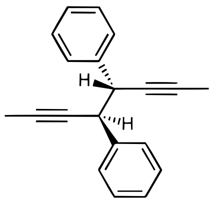
Unlike the previously studied 1,4-bis(pentamethylene)-1,2,3-butatriene,[9,11] 1,1,4,4-tetramethyl-1,2,3-butatriene, and the parent butatriene,[17] this material is stable in the liquid phase and can be purified by conventional means. When dissolved in THF, degassed, and heated at 120 °C for 48 h, a soluble lightly yellow polymer is produced. This solubility is also in contrast to the polymers derived from the monomers mentioned above. The average molecular weights as determined by GPC using polystyrene standards is as follows: M_w =14 kg mol^{-1}, M_n = 8.7 kg mol^{-1}, PD = 1.6. Proton NMR analysis shows the expected aromatic peaks due to the benzene rings and a complex multiplet due to the 1,2-diphenylethylidene unit. Note that these two adjacent centers are both chiral, so that we may have meso or racemic diastereomers at each intermonomer linkage.





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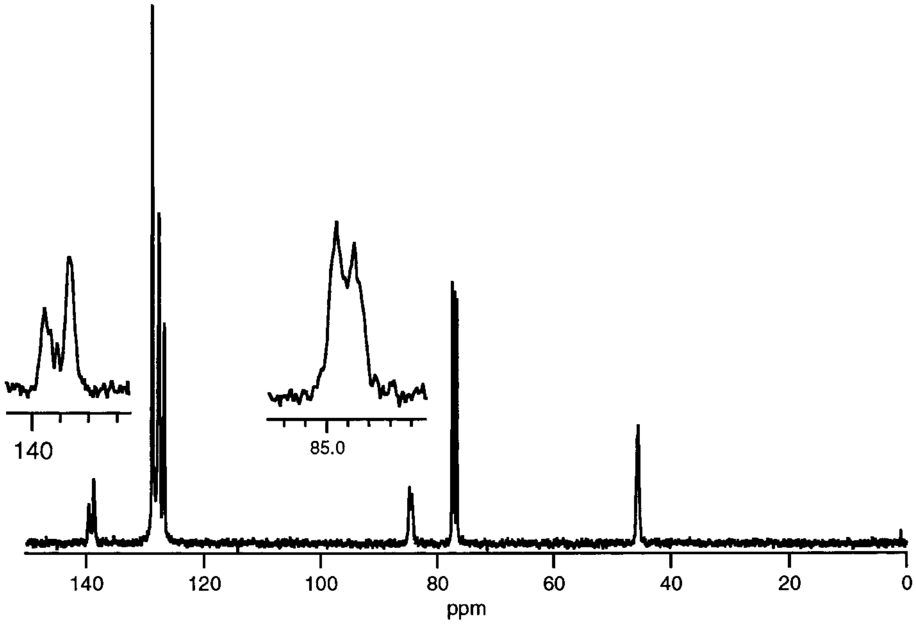


Figure 1. ^{13}C NMR spectrum (in $CDCl_3$) of **2**.

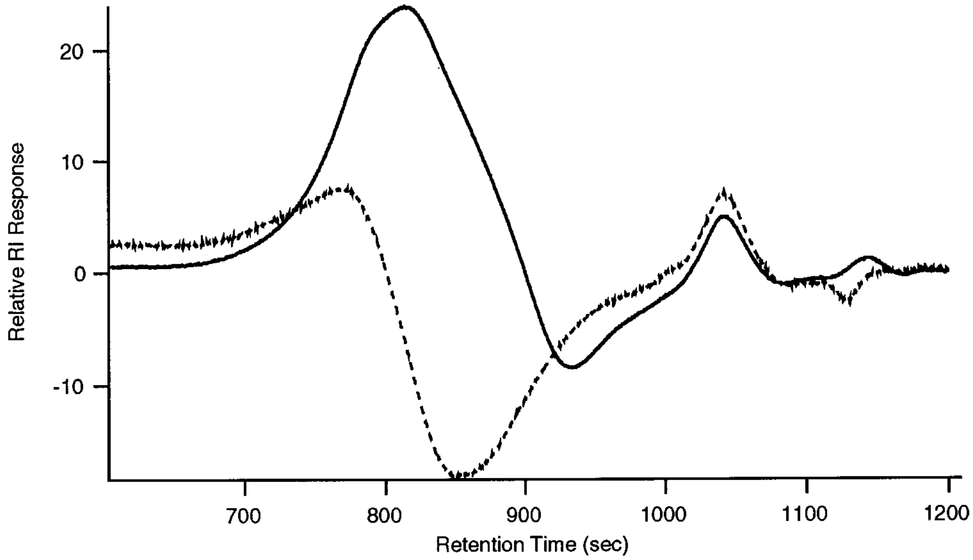
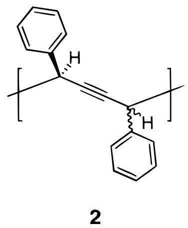


Figure 2. GPC (eluted in toluene) of polymers **2** (dashed) and **3** (solid).

This is borne out in the ^{13}C spectra. We note the presence of two acetylenic peaks at 84.8 and 84.4 ppm as well as two closely spaced peaks in the aromatic region at 139.5 and 138.7 ppm, in addition to the other anticipated resonances for the other sp^2 and sp^3 carbons. Figure 1 shows the ^{13}C NMR spectrum of the initial polymer.

We attribute these splittings to the proximity of the acetylenic and ipso ring carbons to the chiral center in the meso and racemic diastereomers. The relative heights of these split peaks indicate that one of the two diasteromers is preferred, although at this time, we do not have a definitive assignment. Thus, this polymer is atactic. The absence of allenic or vinyl carbons in this spectrum confirms that the polymerization proceeds exclusively via 1,4-addition. The IR spectrum of polymer **2** looks remarkably similar to that of simple polystyrene with the added presence of single acetylenic stretch at 2264 cm^{-1}. Conventional Raman spectroscopy of this materials was attempted, but fluorescence made it difficult to obtain a reasonable spectrum. We are currently studying this and other poly(1,4-butyne-1,4-diyl)s via FT-Raman with excitation at 1047 nm and will report on these studies soon. DSC of the polymer indicated no crystallinity and that it possess a glass transition temperature of 88 °C. Heating this polymer above 200 °C produces a pronounced exotherm. Subsequent heating runs on the now red material show a T_g of 260 °C. This will be discussed further below. In summary, the polymer of **1** is a soluble, atactic, nonconjugated system with the following structure:



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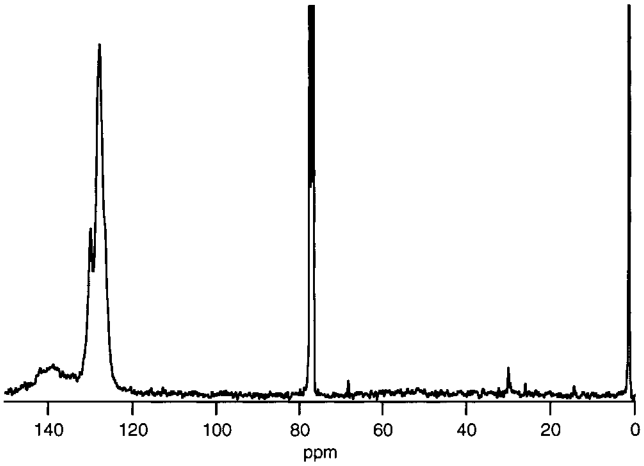


Figure 3. ^{13}C NMR spectrum (in $CDCl_3$) of **3**.

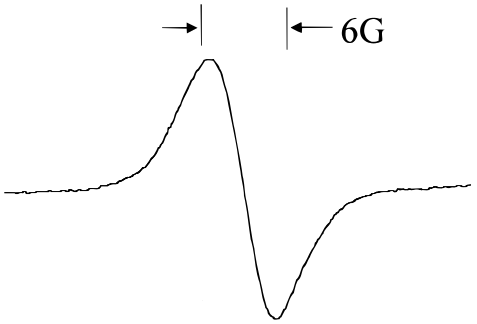


Figure 4. ESR spectrum (in $CHCl_3$) of **3**.

A solution of **2** is light yellow in color. Upon addition of a few drops of saturated potassium *tert*-butoxide in *tert*-butyl alcohol, the solution turns immediately dark red. When allowed to react for 15 min and then precipitated, the resulting material is dark red. GPC of the isolated red polymer shows a shift in molecular weight to higher values ($M_w = 49$ kg mol^{-1}, $M_n = 28$ kg mol^{-1}, PD = 1.8) relative to the molecular weight distribution of the starting polymer **2** (Figure 2)

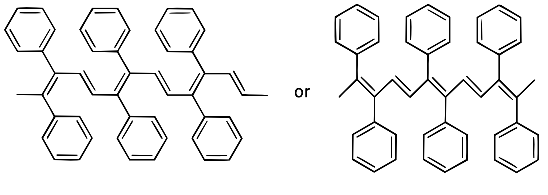
We attribute the inversion of the differential refractive index signal to an increase in the refractive index of polymer after modification. Proton NMR reveals only a single broad peak featureless peak in the aromatic region. Signals due to the benzylic hydrogens are absent. The ^{13}C spectrum is equally simplified (Figure 3).

Both the acetylenic carbons and the benzylic carbons are gone, and only sp^2 type carbons remain. The low field aromatic peaks (assigned to the ipso carbon) at 138.7 and 139.6 ppm (fwhm 0.5 ppm) have coalesced to a broad peak (fwhm 10 ppm) at 138.7 ppm. This, the broadening of the other aromatic carbons and the broad aromatic proton signal, suggested the presence of unpaired spins. The room-temperature ESR spectra of **3** (Figure 4) exhibits a broad Gaussian peak (both in the solid state and in chloroform solution) with $g \sim 2.0$ and $\Delta B_{pp} = 6$ G. ESR line widths for undoped poly(acetylene) have been previously observed in the range 5−10 G at room temperature.[18]

UV/vis spectroscopic comparisons of the polymer before and after treatment with base (Figure 5) shows the growth of a broad new peak centered at approximately 350 nm in addition to the sharper absorption at 254 nm, presumably due to the aromatic rings. The molar absorptivity of **3** is 6 times greater than that of **2** at 350 nm.

In addition, fluorescence measurements of the polymers in chloroform with excitation at 350 nm (Figure 6) give a broad featureless fluorescence peak at 400 nm for **2** which shifts to 480 nm after treatment with base.

DSC data on the treated polymer yields no melting endotherms but does show a glass transition temperature at 260 °C. As mentioned earlier, the untreated polymer exhibits a T_g of 88 °C. Heating either polymer above 300 °C does not increase the T_g beyond the observed 260 °C. These observations are also confirmed by polarized light hot-stage microscopy.



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We attribute these observations to a base-catalyzed (or thermally induced) rearrangement of the nonconjugated **2** to the conjugated poly(acetylenic) form the left isomer being the so-called cis isomer (drawn in the trans−cisoid resonance form) and the right the trans isomer. Such base-catalyzed rearrangements have precedent for 1,5-dynes and other polyynes, although large excesses of base and aggressive conditions must be utilized.[19,20] The introduction of double bonds into the polymer's backbone is consistent with the apparent increase in its molecular weight as observed via GPC analysis due to an increase in chain stiffness and hence its hydrodanmic volume.

It should be noted that the other possible resonance forms for both isomers are not degenerate with those drawn above. The forms drawn above have stilbene-type moieties in the backbone alternating with ethylidene units. The alternative resonance form would have 1,4-diphenyl-1,3-butadiene-moieties. Such is not the case for either poly(acetylene) or the polymers of monosubstituted acetylenes. The breaking of the conjugated backbone's symmetry may impact the electro-optical properties of these polymers, most specifically their potential for exhibiting electroluminescence.

This polymer can be compared with its isomer, poly(1-phenylacetylene). Since the poly(1-phenylacetylene) is substituted on every third backbone carbon, in the trans form, there will be severe steric interaction between phenyl rings on adjacent monomer units, causing this polymer to be nonplanar. As-polymerized poly(1-phenylacetylene) is reported to be a yellow material,[21] indicating a short conjugation length.[22] Conversion to its cis form yields a red material. In the polymer reported in this study, the substituents are more widely spaced and steric interactions should be less severe, leading to longer conjugation lengths.

Conclusions. The molecule 1,4-diphenyl-1,2,3-butatriene can be polymerized thermally to form a soluble poly(2-butyne-1,4-diyl) with relatively high molecular weight. In turn, using mild conditions, this material can be caused to rearrange to a poly(acetylene) with a unique substitution pattern. One can think of the polyacetylene **3** as being the alternating copolymer of acetylene and diphenylacetylene. This substitution pattern for polyacetylene is not readily obtainable by

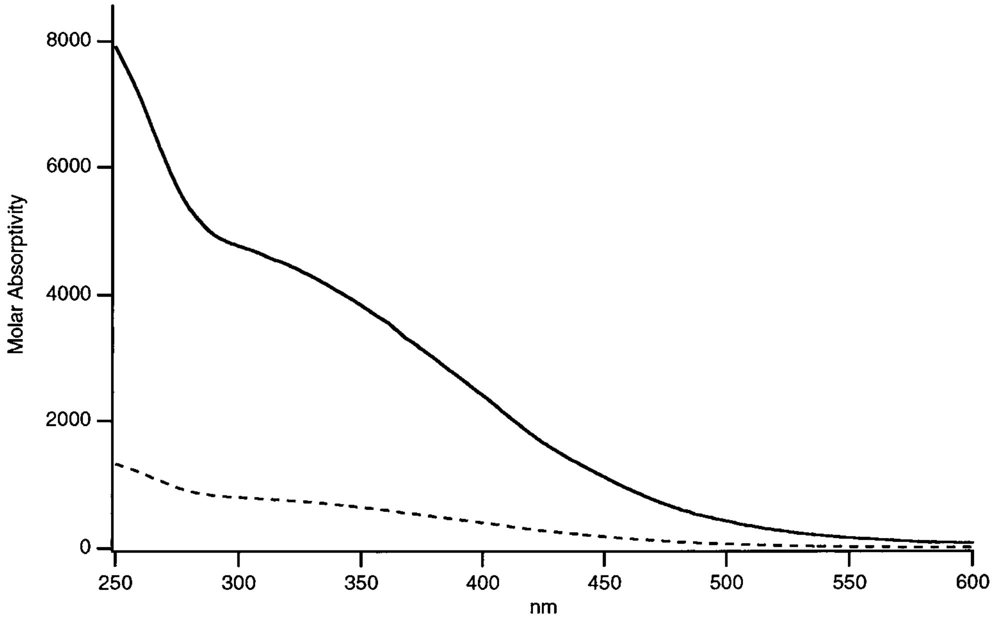

Figure 5. Ultraviolet/visible spectrum (in chloroform) of **2** (0.064 mg/mL, dashed line) and **3** (0.012 mg/mL, solid line).

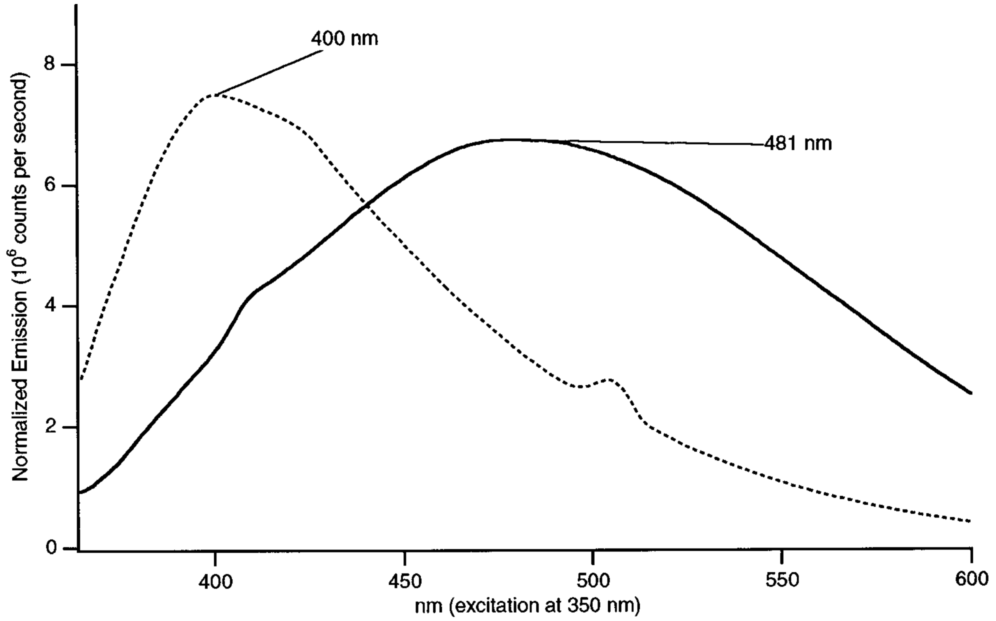

Figure 6. Emission spectrum (in chloroform, excitation at 350 nm) of polymer **2** (dashed line) and **3** (solid line). Both spectra are normalized to their absorbance at 350 nm.

any other route. The ability to utilize substituted benzaldehydes with either electron donating groups or accepting groups in synthesizing the diphenylbutatriene monomer will allow for manipulation of the polymer's electrooptical properties. Ongoing studies in our laboratories are examining the electrooptical and photophysical properties of these systems.

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Supporting Information Available: Text giving experimental procedures and preparations (6 pages). Ordering and access information is given on any current masthead page.

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